

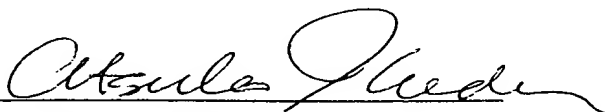


DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/216,517 filed on July 6, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 28th day of September, 2000



Atsuko Ikeda



[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Method and Apparatus for Measuring Fluorocompound
Concentration and Manufacturing Method for
Fluorocompound

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for measuring a hydrofluorocarbon concentration, comprising measuring a concentration of at least one of the hydrofluorocarbons contained in a mixed gas using infrared spectrometry.

[Claim 2] The method for measuring a hydrofluorocarbon concentration as claimed in claim 1, wherein the hydrofluorocarbon concentration in said mixed gas is 8 mol% or less.

[Claim 3] The method for measuring a hydrofluorocarbon concentration as claimed in claim 1 or 2, wherein said mixed gas is a gas containing perfluorocarbon, hydrogen fluoride and/or fluorine gas and the concentration of perfluorocarbon and/or hydrogen fluoride is measured at the same time using infrared spectrometry.

[Claim 4] The method for measuring a hydrofluorocarbon concentration as claimed in claim 3, wherein said mixed gas is rich in perfluorocarbon and/or hydrogen fluoride.

[Claim 5] The method for measuring a hydrofluorocarbon concentration as claimed in any one of claims 1 to 4, wherein the measuring cell is heated and thereby a gas is prevented from condensing on the surface of the measuring cell.

[Claim 6] The method for measuring a hydrofluorocarbon concentration as claimed in claim 5, wherein a purge gas is introduced into the heated measuring cell after the measurement of a gas concentration to remove hydrogen fluoride on the surface of the measuring cell.

[Claim 7] The method for measuring a hydrofluorocarbon concentration as claimed in any one of claims 1 to 6, wherein said hydrofluorocarbon is at least one of the hydrofluorocarbons represented by formula (1):



(wherein x, y and z each represents an integer satisfying the conditions of $1 \leq x \leq 3$, $1 \leq y \leq 4$, $1 \leq z \leq 7$ and $2x+2=y+z$).

[Claim 8] The method for measuring a hydrofluorocarbon concentration as claimed in any one of claims 1 to 7, wherein said hydrofluorocarbon is trifluoromethane, 1,1,1,2-tetrafluoroethane and/or pentafluoroethane, and the concentrations thereof each is measured using a wavenumber in the range from 2,900 to 3,100 cm^{-1} as the measuring wavenumber.

[Claim 9] The method for measuring a hydrofluorocarbon concentration as claimed in any one of claims 3 to 8, wherein said perfluorocarbon is tetrafluoromethane and/or hexafluoroethane, and the concentrations thereof each is measured using a wavenumber in the range from 1,000 to 2,700 cm^{-1} as the measuring wavenumber.

[Claim 10] The method for measuring a hydrofluorocarbon concentration as claimed in any one of claims 3 to 9, wherein the hydrogen fluoride concentration in the mixed gas is measured using a wavenumber in the range from 3,600 to 4,300 cm^{-1} as the measuring wavenumber.

[Claim 11] An apparatus for measuring a hydrofluorocarbon concentration, which is used for the method for measuring a concentration of hydrofluorocarbon contained in a mixed gas described in any one of claims 1 to 10, said apparatus comprising a measuring cell having heating means, an inlet pipeline from which a part of the reaction gas from the production line of perfluorocarbon is sampled, an automatic adjusting change-over valve for introducing a gas, connected to said inlet pipeline and to a purge gas inlet pipeline and capable of adjusting or switching over the amount of the reaction gas and purge gas introduced to said measuring cell, an infrared spectrophotometer, and a data processing device storing a calibration curve.

[Claim 12] The apparatus for measuring a hydrofluorocarbon concentration as claimed in claim 11, wherein an optical window through which an infrared ray in said measuring cell transmits is made of calcium fluoride.

[Claim 13] A method for manufacturing perfluorocarbon, comprising reacting hydrofluorocarbon with fluorine gas in the gaseous phase, wherein the hydrofluorocarbon concentration is adjusted using the measuring method described in any one of claims 1 to 10.

[Claim 14] The method for manufacturing perfluorocarbon as claimed in claim 13, wherein said hydrofluorocarbon concentration is adjusted to 8 mol% or less.

[Claim 15] The method for manufacturing perfluorocarbon as claimed in claim 13 or 14, wherein said hydrofluorocarbon is at least one of the hydrofluorocarbons represented by formula (1):



(wherein x, y and z each represents an integer satisfying the conditions of $1 \leq x \leq 3$, $1 \leq y \leq 4$, $1 \leq z \leq 7$ and $2x+2=y+z$).

[Claim 16] The method for manufacturing perfluorocarbon as claimed in claim 15, wherein said hydrofluorocarbon is at least one selected from the group consisting of trifluoromethane, 1,1,1,2-tetrafluoroethane and pentafluoroethane.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method and an apparatus for measuring a concentration of hydrofluorocarbon contained in a mixed gas using infrared spectrometry, and a method for manufacturing perfluorocarbon using the measuring method.

[0002]

[Background Art]

Perfluorocarbons, for example, tetrafluoromethane and hexafluoroethane, are used as an etching gas or a cleaning gas in the manufacturing process of a semiconductor device. With regard to the manufacturing method for these perfluorocarbons, various methods have heretofore been proposed.

[0003]

For example, in the case of tetrafluoromethane (hereinafter referred to as "FC-14" or " CF_4 "), the following methods are known:

(1) a method of reacting carbon tetrachloride with hydrogen fluoride (hereinafter referred to as "HF") in the presence of a catalyst (see, JP-B-43-10601 (the term "JP-B" as used herein means an "examined Japanese patent

publication"));

(2) a method of reacting dichlorodifluoromethane (CCl_2F_2) or chlorotrifluoromethane (CClF_3) with HF in the presence of a catalyst (see, JP-B-42-3004 and JP-B-62-10211);

(3) a method of reacting trifluoromethane (CHF_3) with fluorine gas (hereinafter referred to as " F_2 ") (see, GB-1116920);

(4) a method of reacting carbon (C) with F_2 in BrF_3 or IF_5 (see, JP-A-58-162536) (the term "JP-A" as used herein means an "unexamined published Japanese patent application"); and

(5) a method of thermally decomposing tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) and CO_2 at a high temperature (see, U.S. Patent 4,365,102).

[0004]

For example, in the case of hexafluoroethane (hereinafter referred to as "FC-116" or " CF_3CF_3 "), the following methods are known:

(6) an electrolytic fluorination method using ethane and/or ethylene as a starting material;

(7) a method of thermally decomposing tetrafluoroethylene or the like;

(8) a method of fluorinating acetylene, ethylene

and/or ethane using a metal fluoride;

(9) a method of fluorinating dichlorotetrafluoroethane, chloropentafluoroethane or the like using HF in the presence of a catalyst; and

(10) a method of reacting ethane or the like with F_2 .

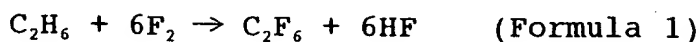
[0005]

These methods have the following problems. In the methods (1), (2) and (9), a large amount of hydrochloric acid is produced as a by-product and a high temperature is necessary; in the methods (5) and (7), a high decomposition temperature is necessary and the yield is low; in the method (6), many side reactions take place and the separation or purification of the product has a problem; and in the method (8), the metal fluoride must be regenerated by F_2 and the consumption of fluorine is large.

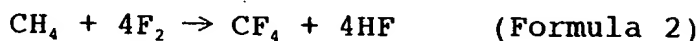
[0006]

In the direct fluorination method using F_2 of the method (3) or (10), the F_2 used is extremely rich in reactivity and therefore, there is a danger of explosion between the organic compound substrate and F_2 , or corrosion or the like, moreover, the side reaction is also dangerous, such as cleavage of the C-C bond or polymerization due to the generation of heat, or abrupt reaction or explosion resulting from production, deposition or the like of carbon.

For example, in the case of producing a perfluorocompound by the direct fluorination method using a straight-chain hydrocarbon and F_2 , a huge heat of reaction is generated as follows:



$$(\Delta H = -690 \text{ kcal/mol})$$



$$(\Delta H = -479 \text{ kcal/mol})$$

[0007]

In order to solve these problems, various methods have been studied and, for example, the following methods are known:

(1) a method of reacting ethane with F_2 by a jet reactor to obtain FC-14 or FC-116, where nitrogen is used as the diluting gas (see, J. Amer. Chem. Soc., 77, 3307 (1955), and J. Amer. Chem. Soc., 82, 5827 (1960));

(2) a method of fluorinating C-H by F_2 in a reactor having a porous alumina tube (see, EP31519);

(3) a method of fluorinating a straight-chain hydrocarbon with F_2 in the presence of a diluting gas in a reactor having a porous metal tube (double tube structure), where SF_6 , CF_4 , C_2F_6 or C_3F_8 is used as the diluting gas (see, EP32210); and

(4) a method of reacting a saturated or unsaturated

hydrocarbon or a partially fluorinated hydrocarbon with F_2 to produce hydrofluorocarbon (see, U.S. Patent 5,406,008), or a method of producing fluorinated alkene from alkene and carbon containing F_2 by adsorption (see, JP-A-2-207052).

However, these methods cannot be necessarily satisfied in attaining the object of realizing a safe and efficient manufacture of perfluorocarbon.

[0008]

Furthermore, (5) a method of reacting a hydrofluorocarbon with F_2 in the gaseous phase at an elevated temperature in the presence of a diluting gas (see, JP-A-9-241186 and JP-A-9-241187) has been proposed. According to these methods, hydrofluorocarbons are adjusted to a concentration of 8 mol% or less using a diluting gas at the inlet of a reactor and reacted with F_2 at an elevated temperature, so that perfluorocarbon can be safely and efficiently produced.

[0009]

For safely performing the above-described direct fluorination reaction, it is necessary to exactly and rapidly analyze and control the concentration of hydrofluorocarbons at the inlet of a reactor. According to the method heretofore commonly used for quantitating hydrofluorocarbons in a gas flow at the inlet of a reactor,

a part of a mixed gas is extracted and washed with a potassium iodide solution, thereafter, (1) a part of the washing solution is sampled and subjected to iodometry or alkalimetry to quantitate the acidic gas components such as HF or F₂ and (2) the washed gas is analyzed by gas chromatography to quantitate hydrofluorocarbons, perfluorocarbons and other trace gas components.

[0010]

This analysis method has, however, a problem in that a long time is necessary from the start of an operation of extracting a mixed gas until the analysis results are obtained and this is deficient for controlling the reaction and also in that the operation of extracting a mixed gas and the iodometry or alkalimetry must be done by hand and workers are inevitably obliged to handle a substance containing HF or F₂ which is a dangerous corrosive gas.

[0011]

[Problems to be Solved by the Invention]

The present invention has been made under these circumstances and the object of the present invention is to provide a method for manufacturing perfluorocarbon using a direct fluorination reaction of reacting hydrofluorocarbon with F₂, where the concentration of hydrofluorocarbons in a mixed gas flow can be safely analyzed within a short time.

[0012]

[Means to Solve the Problems]

As a result of extensive investigations to solve the above-described problems, the present inventors have found that in the method of manufacturing perfluorocarbons by reacting a hydrofluorocarbon with fluorine gas, the concentration of hydrofluorocarbons contained in a mixed gas flow can be quantitated by introducing a part of the mixed gas flow into a measuring cell and measuring it using infrared spectrometry. The present invention has been accomplished based on this finding. The present invention provides a method and an apparatus for measuring a hydrofluorocarbon concentration in a mixed gas and also a manufacturing method for fluorocompound, described in (1) to (16) below.

[0013]

(1) A method for measuring a hydrofluorocarbon concentration, comprising measuring a concentration of at least one of the hydrofluorocarbons contained in a mixed gas using infrared spectrometry.

(2) The method for measuring a hydrofluorocarbon concentration as described in (1) above, wherein the hydrofluorocarbon concentration in the mixed gas is 8 mol% or less.

(3) The method for measuring a hydrofluorocarbon concentration as described in (1) or (2) above, wherein the mixed gas is a gas containing perfluorocarbon, hydrogen fluoride and/or fluorine gas and the concentration of perfluorocarbon and/or hydrogen fluoride is measured at the same time using infrared spectrometry.

(4) The method for measuring a hydrofluorocarbon concentration as described in (3) above, wherein the mixed gas is rich in perfluorocarbon and/or hydrogen fluoride.

(5) The method for measuring a hydrofluorocarbon concentration as described in any one of (1) to (4) above, wherein the measuring cell is heated and thereby a gas is prevented from condensing on the surface of the measuring cell.

[0014]

(6) The method for measuring a hydrofluorocarbon concentration as described in (5) above, wherein a purge gas is introduced into the heated measuring cell after the measurement of a gas concentration to remove hydrogen fluoride on the surface of the measuring cell.

(7) The method for measuring a hydrofluorocarbon concentration as described in any one of (1) to (6) above, wherein the hydrofluorocarbon is at least one of the hydrofluorocarbons represented by formula (1):



(1)

(wherein x, y and z each represents an integer satisfying the conditions of $1 \leq x \leq 3$, $1 \leq y \leq 4$, $1 \leq z \leq 7$ and $2x+2=y+z$).

(8) The method for measuring a hydrofluorocarbon concentration as described in any one of (1) to (7) above, wherein the hydrofluorocarbon is trifluoromethane, 1,1,1,2-tetrafluoroethane and/or pentafluoroethane, and the concentrations thereof each is measured using a wavenumber in the range from 2,900 to 3,100 cm^{-1} as the measuring wavenumber.

(9) The method for measuring a hydrofluorocarbon concentration as described in any one of (3) to (8) above, wherein the perfluorocarbon is tetrafluoromethane and/or hexafluoroethane, and the concentrations thereof each is measured using a wavenumber in the range from 1,000 to 2,700 cm^{-1} as the measuring wavenumber.

(10) The method for measuring a hydrofluorocarbon concentration as described in any one of (3) to (9) above, wherein the hydrogen fluoride concentration in the mixed gas is measured using a wavenumber in the range from 3,600 to 4,300 cm^{-1} as the measuring wavenumber.

[0015]

(11) An apparatus for measuring a hydrofluorocarbon concentration, which is used for the method for measuring a

concentration of hydrofluorocarbon contained in a mixed gas described in any one of (1) to (10), the apparatus comprising a measuring cell having heating means, an inlet pipeline from which a part of the reaction gas from the production line of perfluorocarbon is sampled, an automatic adjusting change-over valve for introducing a gas, connected to the inlet pipeline and to a purge gas inlet pipeline and capable of adjusting or changing over the amount of the reaction gas and purge gas introduced to the measuring cell, an infrared spectrophotometer, and a data processing device storing a calibration curve.

(12) The apparatus for measuring a hydrofluorocarbon concentration as described in (11) above, wherein an optical window through which an infrared ray in the measuring cell transmits is made of calcium fluoride.

(13) A method for manufacturing perfluorocarbon, comprising reacting hydrofluorocarbon with fluorine gas in the gaseous phase) above, wherein the hydrofluorocarbon concentration is adjusted using the measuring method described in any one of (1) to (10).

(14) The method for manufacturing perfluorocarbon as described in (13) above, wherein the hydrofluorocarbon concentration is adjusted to 8 mol% or less.

(15) The method for manufacturing perfluorocarbon as

described in (13) or (14) above, wherein the hydrofluorocarbon is at least one of the hydrofluorocarbons represented by formula (1):



(wherein x, y and z each represents an integer satisfying the conditions of $1 \leq x \leq 3$, $1 \leq y \leq 4$, $1 \leq z \leq 7$ and $2x+2=y+z$).

(16) The method for manufacturing perfluorocarbon as described in (15) above, wherein the hydrofluorocarbon is at least one selected from the group consisting of trifluoromethane, 1,1,1,2-tetrafluoroethane and pentafluoroethane.

[0016]

That is, the present invention is "a method for measuring a hydrofluorocarbon concentration, comprising measuring a concentration of at least one of the hydrofluorocarbons contained in a mixed gas using infrared spectrometry", "an apparatus used for the measuring method" and "a manufacturing method for perfluorocarbon, wherein the hydrofluorocarbon concentration is controlled using the measuring method".

[0017]

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

The present invention is characterized in that in the

method of manufacturing perfluorocarbon using a direct fluorination reaction of reacting hydrofluorocarbons with fluorine gas, the concentration of at least one of the hydrofluorocarbons contained in a mixed gas is measured using infrared spectrometry. In the mixed gas, at least one of perfluorocarbon, hydrogen fluoride and fluorine gas may be contained in addition to the hydrofluorocarbon, and the perfluorocarbon and hydrogen fluoride can also be measured at the same time using the infrared spectrometry in the same manner as the hydrofluorocarbon.

[0018]

The hydrofluorocarbon is at least one of the hydrofluorocarbons represented by the formula (1):



(x, y and z each represents an integer satisfying the conditions of $1 \leq x \leq 3$, $1 \leq y \leq 4$, $1 \leq z \leq 7$ and $2x+2=y+z$), preferably trifluoromethane, 1,1,1,2-tetrafluoroethane and/or pentafluoroethane.

[0019]

The perfluorocarbon is at least one compound selected from the group consisting of tetrafluoromethane, hexafluoroethane and octafluoropropane, preferably tetrafluoromethane and/or hexafluoroethane.

[0020]

In the measuring method of the present invention, the hydrofluorocarbon concentration can be adjusted to an arbitrary ratio as well as HF and perfluorocarbon. However, as described above, the reaction of an organic compound with F_2 involves generation of huge heat of reaction and if the hydrofluorocarbons as the reaction substrate contact with fluorine, combustion or explosion may occur. For example, the lower limit of the range of causing explosion between hydrofluorocarbons and F_2 is known to be about 6% in the case of pentafluoroethane and about 4% in the case of 1,1,1,2-tetrafluoroethane. Thus, the mixture composition is limited so as to allow the reaction to proceed safely.

[0021]

For introducing a mixed gas into a measuring cell, a method of continuously introducing the reaction gas or a method of continuously extracting the reaction gas from the reaction apparatus using a change-over valve is preferred. The measuring cell may be provided in two or more series so as to reduce the analysis time. The change-over valve can be switched over by any arbitrary method, however, an automatic adjusting change-over valve using an electrical driving force or a pneumatic driving force is preferred. The change-over valve may be switched over at the timing

controlled by a control device in which the change-over program is stored. The change-over valve, the inlet piping for introducing a gas into the measuring cell, and the measuring cell are preferably heated so as to prevent condensation of the mixed gas. The temperature range therefor is preferably 20°C or more, more preferably 30°C or more. The pipeline and the measuring cell which are not used for the analysis may be purged by a clean dry gas or may be preliminarily substituted by the mixed gas.

[0022]

The wavelength used at the time of measuring respective gas components contained in the mixed gas using infrared spectrometry varies according to the gas component and a preferred wavelength can be selected for each component. For the hydrofluorocarbon, a wavenumber selected from the range of 2,900 to 3,100 cm^{-1} which is considered attributable to the C-H stretching vibration may be used. For example, in the case of measuring the trifluoromethane concentration, a wavelength of 3,033 to 3,037 cm^{-1} can be used, in the case of 1,1,1,2-tetrafluoroethane, a wavelength of 2,981 to 2,986 cm^{-1} or 3,011 to 3,014 cm^{-1} , and in the case of pentafluoroethane, a wavelength of 2,996 to 3,006 cm^{-1} , however, the measuring wavelength is not limited thereto.

[0023]

For perfluorocarbon, a wavenumber selected from the range of 11,000 to 2,700 cm^{-1} which is considered attributable to the C-F stretching or deformation vibration may be used. For example, in the case of measuring the tetrafluoromethane concentration, a wavelength of 1,500 to 1,535 cm^{-1} , 1,535 to 1,540 cm^{-1} , 1,540 to 1,585 cm^{-1} , 2,120 to 2,150 cm^{-1} or 2,150 to 2,210 cm^{-1} can be used, and in the case of hexafluoroethane, a wavelength of 1,420 to 1,490 cm^{-1} , 1,570 to 1,670 cm^{-1} , 2,030 to 2,080 cm^{-1} , 2,300 to 2,380 cm^{-1} or 2,630 to 2,690 cm^{-1} , however, the wavelength is not limited thereto.

[0024]

Similarly, in the case of measuring the hydrogen fluoride concentration in a mixed gas, a wavenumber selected from the range of 3,600 to 4,300 cm^{-1} may be used. For example, a wavelength of 4,160 to 4,190 cm^{-1} , 4,190 to 4,220 cm^{-1} , 4,220 to 4,240 cm^{-1} , 4,245 to 4,270 cm^{-1} or 4,270 to 4,290 cm^{-1} can be used, but the wavelength is not limited thereto.

[0025]

The measuring apparatus of the present invention is described below.

Fig. 1 is a schematic view of an analysis apparatus

according to one practical embodiment of the present invention. In the figure, 7 is a measuring cell equipped with heating means; 6 is an automatic adjusting change-over valve for introducing a gas, connected to an inlet pipeline 1 from which a part of the reaction gas from the production line of perfluorocarbon is sampled, and to a purge gas inlet pipeline 2 so as to introduce the reaction gas and a purge gas into the measuring cell 7; 8 indicates an infrared measuring apparatus; 3 is an inlet pipeline for introducing the reaction gas and a purge gas into the measuring cell 7; and 4 is an outlet pipeline for the gas introduced into the measuring cell 7.

[0026]

The reaction gas and purge gas is introduced into the measuring cell 7 by changing the setting of the automatic adjusting change-over valve 6 and the exhaust gas passed through the outlet pipeline 4 is discharged out of the system through the poison-removing line 5. At the time of measuring the concentration of a reaction gas component, the gas is passed until the reaction gas in the measuring cell reaches a constant concentration and then, the gas is enclosed by closing the inlet and outlet of the cell. After the completion of measurement, the gas components condensed on the surface of the measuring cell are preferably removed

by sufficiently passing a purge gas, however, the next measurement may be performed by passing the reaction gas until the reaction gas in the measuring cell reaches a constant concentration and then enclosing the gas. In either case, the measuring cell is preferably heated at 20°C or more.

[0027]

In the measuring apparatus of the present invention, the automatic adjusting change-over valve 6, the gas pipelines 1 to 5 and the measuring cell preferably have corrosion resistance against HF and F₂. For the metal material, SUS, Monel or Inconel is preferred, and for the optical material (window material of the measuring cell), a metal halide which transmits the infrared wavelength light used for the analysis is preferred. Examples of the metal halide include lithium fluoride, sodium fluoride, calcium fluoride, magnesium fluoride, strontium fluoride and barium fluoride. Among these, calcium fluoride is preferred.

[0028]

The infrared spectrophotometer is preferably a Fourier transform infrared spectrophotometer. The data processing device stores a calibration curve and performs the quantitation of hydrofluorocarbons, perfluorocarbons and/or hydrogen fluoride based on the measurement results obtained

by an analyzer. A device having a function of converting the quantitation results into electrical signals and displaying the results on another displaying device may also be used.

[0029]

The method of manufacturing perfluorocarbon while adjusting the hydrofluorocarbon concentration using the measuring method of the present invention is described below.

Fig. 2 is a schematic view showing the production flow of fluorocompound according to one practical embodiment of the present invention. In this embodiment, the flow shows the production of one compound or different two compounds in a production plant having two reaction zones. In Fig. 2, 11 is a first reaction zone where fluorine gas fed from 14 and hydrofluorocarbon fed from 15 are reacted; 12 is a second reaction zone where using the reaction gas produced in the first reaction zone as the diluting gas, fluorine gas fed from 18 and hydrofluorocarbon fed from 19 are reacted; 21 is an outlet gas of the second reaction zone and a part 23 thereof is introduced into the distillation and purification step and the remaining 22 is circulated and reused as the diluting gas in the first reaction zone and/or the second reaction zone; and 24 and 25 each is an

infrared measuring apparatus shown in Fig. 1 and provided before each of the first reaction zone and the second reaction zone to measure the hydrofluorocarbon concentration. The infrared measuring apparatuses 24 and 25 may be provided after each of the first reaction zone 11 and the second reaction zone 12 and in this case, the concentration of residual hydrofluorocarbon can be measured.

[0030]

The above-described hydrofluorocarbon is at least one of the hydrofluorocarbons represented by formula (1):



(wherein x, y and z each represents an integer satisfying the conditions of $1 \leq x \leq 3$, $1 \leq y \leq 4$, $1 \leq z \leq 7$ and $2x+2=y+z$), preferably trifluoromethane, 1,1,1,2-tetrafluoroethane or pentafluoroethane.

[0031]

In reacting these hydrofluorocarbons with fluorine gas, it is necessary that the composition of the mixed gas does not fall within the range of explosion and although the value may vary depending on the kind of the compound, the composition ratio of each compound is set to the safe range below the lower limit of the explosion range.

[0032]

[Examples]

The present invention is described in greater detail below by referring to the Examples, however, the present invention is not limited to these Examples.

(Example 1)

An Inconel 600-made reactor having an inside diameter of 20.6 mm ϕ and a length of 500 mm (using a heating system by an electric heater; a passivation treatment was already practiced at a temperature of 600°C using fluorine gas) was heated to 280°C while passing a diluting gas comprising 41.8 vol% of tetrafluoromethane as perfluorocarbon and 58.2 vol% of hydrogen fluoride, at 50 NL/h. To one gas flow diverged from the diluting gas, 1,1,1,2-tetrafluoroethane as hydrofluorocarbon was passed at 1.0 NL/h. Thereafter, to another gas flow similarly diverged from the diluting gas, fluorine gas was fed at 2.0 NL/h and a direct fluorination reaction was performed. A part of the reactor inlet gas was introduced into a heated measuring cell (window material: calcium fluoride) by a pneumatic driving force-type automatic adjusting change-over valve made of SUS 316 and the infrared absorption spectrum was measured by an infrared spectrophotometer.

[0033]

The wavelength of the infrared absorption spectrum for measuring a concentration of each compound is shown in Table 1.

[Table 1]

| Name of Compound | Wavelength |
|---------------------------|--|
| Trifluoromethane | 3,033 to 3,037 cm^{-1} |
| 1,1,1,2-Tetrafluoroethane | 2,981 to 2,986 cm^{-1} or 3,011 to 3,014 cm^{-1} |
| Pentafluoroethane | 2,996 to 3,006 cm^{-1} |
| Tetrafluoromethane | 1,542 to 1,585 cm^{-1} |
| Hexafluoroethane | 2,630 to 2,690 cm^{-1} |
| Hydrogen fluoride | 4,228 to 4,235 cm^{-1} |

[0034]

The amounts of components contained in the reactor inlet gas were quantitated and the results obtained are shown in Table 2.

[Table 2]

| Name of Compound | Measurement Results |
|---------------------------|---------------------|
| Trifluoromethane | <0.1 vol% |
| 1,1,1,2-Tetrafluoroethane | 2.0 vol% |
| Pentafluoroethane | <0.1 vol% |
| Hexafluoroethane | <0.1 vol% |
| Tetrafluoromethane | 39.2 vol% |
| Hydrogen fluoride | 54.8 vol% |

[0035]

(Example 2)

Using a mixed gas having the composition described in Example 1, a direct fluorination reaction was performed at a reactor temperature of 280°C. The reactor outlet gas was analyzed in the same manner as in Example 1 and the results obtained are shown in Table 3.

[Table 3]

| Name of Compound | Measurement Results |
|---------------------------|---------------------|
| Trifluoromethane | <0.1 vol% |
| 1,1,1,2-Tetrafluoroethane | <0.1 vol% |
| Pentafluoroethane | 0.3 vol% |
| Hexafluoroethane | 1.7 vol% |
| Tetrafluoromethane | 39.3 vol% |
| Hydrogen fluoride | 58.7 vol% |

[0036]

(Comparative Example 1)

A mixed gas having the composition described in Example 1 was analyzed by a conventional method. The reactor inlet gas was washed with a potassium iodide solution and the gas was passed until the amount of the outlet gas of the gas washing bottle reached 5 L. After the gas washing bottle and the inside of the gas meter for measuring the gas amount were thoroughly displaced by the

washed gas, the washed gas was collected in a fluororesin-made bag. A part of the washing solution was sampled and subjected to alkalimetry and iodometry to quantitate hydrogen fluoride and F_2 in the mixed gas. Also, a part of the washed gas was sampled and the gas components were quantitated by gas chromatography.

The concentrations of the acidic gas component and each fluorocompound were almost agreed with the results in Example 1 as shown in Table 4 but a time period of 1 hour and 30 minutes was necessary from the sampling of the reactor inlet gas until the coming out of all analysis results.

[0037]

[Table 4]

| Name of Compound | Measurement Results |
|---------------------------|---------------------|
| Trifluoromethane | <0.1 vol% |
| 1,1,1,2-Tetrafluoroethane | 2.0 vol% |
| Pentafluoroethane | <0.1 vol% |
| Hexafluoroethane | <0.1 vol% |
| Tetrafluoromethane | 39.3 vol% |
| Hydrogen fluoride | 54.7 vol% |
| Fluorine gas | 4.0 vol% |

[0038]

(Example 3)

A reaction was performed under the same conditions as in Example 1. The reactor outlet gas was introduced into the measuring cell using a sample-introducing system equipped with an automatic adjusting change-over valve and the gas components were quantitated every 15 minutes. Out of the gas components, HFC-125 and HFC-134a of which concentrations are particularly necessary to control so as to evade the danger of combustion or explosion, were measured and the results are shown in Table 5. The measurement results revealed that these two components both were continuously stable.

[0039]

[Table 5]

| Time Passed (min) | HFC-125 (vol%) | HFC-134a (vol%) |
|-------------------|----------------|-----------------|
| 15 | <0.1 | <0.1 |
| 30 | 0.1 | <0.1 |
| 45 | 0.2 | <0.1 |
| 60 | <0.1 | <0.1 |
| 75 | <0.1 | <0.1 |
| 90 | 0.3 | <0.1 |
| 105 | 0.2 | <0.1 |
| 120 | 0.1 | <0.1 |
| 135 | <0.1 | <0.1 |
| 150 | <0.1 | <0.1 |

[0040]

[Effects of the Invention]

As described in the foregoing pages, according to the measuring method of the present invention, in the direct fluorination reaction using hydrofluorocarbon as the reaction substrate and F_2 , the hydrofluorocarbons, perfluorocarbons and/or hydrogen fluoride in a mixed gas flow can be safely quantitated within a short time.

[BRIEF DESCRIPTION OF DRAWINGS]

[Fig. 1]

Fig. 1 is a schematic view showing an apparatus for measuring the concentration of hydrofluorocarbons according to one embodiment of the present invention.

[Fig. 2]

Fig. 2 is a schematic view showing the production flow of perfluorocarbon according to one embodiment of the present invention.

[Description of Reference Numerals]

- 1 reaction gas inlet pipeline
- 2 purge gas inlet pipeline
- 3 gas inlet pipeline
- 4 gas outlet pipeline
- 5 poison-removing line
- 6 automatic adjusting change-over valve for introducing

gas

- 7 measuring cell
- 8 infrared measuring apparatus
- 11 first reaction zone
- 12 second reaction zone
- 13 distillation and purification step
- 14 fluorine gas fed to first reaction zone
- 15 hydrofluorocarbon fed to first reaction zone
- 16 gas components fed to first reaction zone
- 17 outlet gas components of first reaction zone
- 18 fluorine gas fed to second reaction zone
- 19 hydrofluorocarbon fed to second reaction zone
- 20 gas components fed to second reaction zone
- 21 outlet gas components of second reaction zone
- 22 diluting gas
- 23 gas introduced to distillation and purification step
- 24 infrared measuring apparatus 1
- 25 infrared measuring apparatus 2

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a method capable of rapid, easy and highly precision measurement necessary for controlling the hydrofluorocarbon concentration to fall within the predetermined range in a plant of manufacturing perfluorocarbon.

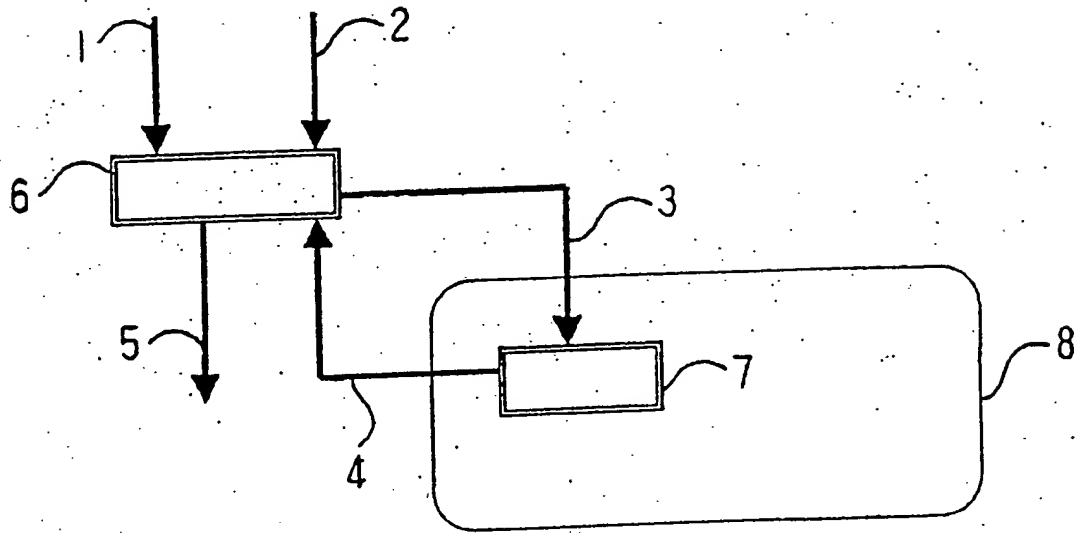
[MEANS TO SOLVE THE PROBLEM]

A method of measuring the concentration of at least one hydrofluorocarbon contained in a mixed gas using infrared spectrometry.

[SELECTED DRAWING] None

[NAME OF THE DOCUMENT] Drawing

[Fig. 1]



[Fig. 2]

